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(54) **Polyorganosiloxane fine particles**

(57) Polyorganosiloxane fine particles represented by the average composition formula,



wherein R represents a substituted or unsubstituted monovalent hydrocarbon group, and a and b are numbers defined by the formulae  $1 < a \leq 1.7$ ,  $1 < b < 1.5$  and  $a + 2b = 4$ , the fine particles having an average particle diameter of from 0.01 to 100  $\mu\text{m}$ , and being of spherical form.

The particles are obtained by (1) cohydrolysing a mixture of silanes  $R_2Si(OR)_2$  and  $R Si(OR)_3$  in the presence of organic acid and then (2) further condensing the product in an aqueous alkali solution.

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## POLYORGANOSILOXANE FINE PARTICLES

The present invention relates to polyorgano-siloxane fine particles which are spherical and have small average particle diameter, and uniform and homogeneous composition.

Known as fine particles having a siloxane bond are fine particles of silicas such as fumed silica, precipitated silica and ground quartz. The silica fine particles are used as additives for various purposes, such as for thickening various plastics, imparting thixotropy to various plastics, preventing the aggregation of pigments, reinforcing organic rubbers, reducing liquids to fine particles (useful fine particles impregnated with liquids), preventing the blocking of films, deluster of coating material, preventing the aggregation of toners and regulating the electric charges of toners.

However, the silica fine particles have an average composition formula of  $\text{SiO}_2$  and a high true specific gravity (hereinafter referred to as "specific gravity" for simplicity) of about 2.0, so that where they are used in the form of a dispersion or the like, precipitation separation thereof tends to occur.

Further, since the silica fine particles have a high hydrophilicity, they have a poor compatibility with various plastics, making it difficult to blend the particles with the plastics, and also the particles are not suitable for the purpose of use where water resistance is required.

For the purpose of improving the compatibility and water resistance, a process for producing fine particles having hydrophobicity has been proposed. JP-A-63-6062 discloses a method for treating silica fine powder with a polyorganosiloxane having a hydrolyzable group or a halogen atom at both terminals thereof, and an organosilicon compound, and JP-A(PCT)-57-500738 discloses a process for producing silica fillers by mixing an alkyl silicate, water which completely hydrolyzes an alkoxy group in the alkyl silicate, an alcohol, and a hydrophobicizing agent as a trialkylsilylating agent of an organosilicon compound in the presence of a basic catalyst. (The terms "JP-A" and JP-A(PCT) as used herein mean as "unexamined published Japanese patent application" and an "unexamined published Japanese patent application in PCT", respectively.) However, the fine particles obtained by those methods are particles obtained by surface treating inorganic silica powder with a silicon compound. Therefore, the fine particles obtained by such production methods have still the disadvantage that the specific gravity thereof is high. In addition, the process disclosed in the above-described JP-A(PCT)-57-500738 is a complicated process in that the hydrophobicizing agent for the

organosilicon compound must be added prior to occurrence of gelation during hydrolysis of the alkyl silicate; and also suffers the problem that it is difficult to obtain fine particles having a homogeneous particle constitution and stable properties.

The following methods have been proposed as methods for obtaining rubber-like fine particles having hydrophobicity and a reduced specific gravity: JP-A-59-68333 discloses a method in which a curable polyorganosiloxane composition is atomized in hot air for curing; JP-A-62-243621 discloses a method in which an addition cure-type liquid silicone rubber composition is emulsified in water and the resulting emulsion is then dispersed into hot water at 25°C or more, thereby to cure the dispersed composition into particles; and JP-A-63-17959 discloses a method in which the structural components of the addition cure-type liquid silicone rubber composition as described in the above JP-A-62-243621 are mixed at a low temperature of -60°C to +5°C and then atomized in hot air, thereby to cure the composition in the atomized state.

However, it is difficult by these methods to obtain fine particles with a homogeneous constitution and having a small average particle diameter of a micron order, or fine particles having uniformly spherical particle shape. Therefore, the particles have the disadvantage that a uniform dispersion is difficult

to obtain when being blended with plastics, and they cannot suitably be used to add to a film or the like.

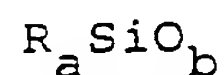
The present inventors previously found that, as fine particles having a siloxane bond, polymethylsilsesquioxane particles having excellent fluidity and which are uniformly spherical can be obtained by hydrolysis condensing a methyltrialkoxysilane in an aqueous solution of ammonia, an amine or the like (see, for example, JP-A-60-13813 and JP-A-63-77940).

Although the fine particles obtained by this method have a specific gravity of about 1.32 and a uniform particle shape, they have poor elasticity. Therefore, problems tend to occur in that, when the particles are applied to delicate materials to be sealed, such as semi-conductors, the particles break the materials or the particles per se cannot be deformed by pressure, and as a result, the particles crack through concentration of stress. Further, it has not yet been possible to achieve fine particles having a controllable compatibility with various plastics or a controllable refractive index by introducing organic groups other than a methyl group, or which can be modified by introduction of a reactive group.

The present inventors have conducted intensive studies into obtaining polyorganosiloxane fine particles having a low specific gravity, small average particle diameter, sphericity, hydrophobicity or various organic

groups introduced therein, homogeneous composition and uniform particle size, taking into consideration the process previously proposed by the present inventors in JP-A-1-217039. As a result, they have found that the desired polyorganosiloxane fine particles can be obtained by hydrolyzing two kinds of alkoxysilanes in the presence of an organic acid to obtain two corresponding organosilanols and/or partial condensates of these hydrolyzates, subjecting the same to polycondensation reaction to form particles, and then drying the particles.

According to the present invention there are provided polyorganosiloxane fine particles whose average composition is represented by the formula



wherein R represents a substituted or unsubstituted monovalent hydrocarbon group, and a and b are numbers defined by the formulae  $1 < a \leq 1.7$ ,  $1 < b < 1.5$  and  $a + 2b = 4$ , the fine particles having an average particle diameter of from 0.10 to 100  $\mu\text{m}$ , and being of spherical form.

In the above average composition formula, examples of the substituted or unsubstituted monovalent hydrocarbon group include an alkyl group such as methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, nonyl, decyl or dodecyl; a cycloalkyl group such as cyclohexyl; an aralkyl group such as 2-phenylpropyl; an aryl group such as phenyl or tolyl; an alkenyl group such as vinyl or allyl; and a substituted

hydrocarbon group such as chloromethyl,  $\gamma$ -chloropropyl,  $\gamma$ -methacryloxypropyl,  $\gamma$ -glycidoxypropyl, 3,4-epoxycyclohexylethyl,  $\gamma$ -mercaptopropyl,  $\gamma$ -aminopropyl, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyl or 3,3,3-trifluoropropyl. The hydrocarbon groups bonded to the silicon atoms may be of one or more kinds.

The polyorganosiloxane fine particles of this invention preferably have an average particle diameter of from 0.01 to 20  $\mu$ m.

According to the present invention the polyorganosiloxane fine particles of the above formula are obtained by a process which comprises the steps of:

(Step 1) partially or completely hydrolyzing a mixture of an organotrialkoxysilane represented by the formula (I)



wherein  $R^1$  represents a substituted or unsubstituted monovalent hydrocarbon group and  $R^2$  represents a substituted or unsubstituted alkyl group, and a diorganodialkoxysilane represented by the formula (II)



wherein  $R^1$  and  $R^2$  are the same as defined above, in the presence of an organic acid to obtain an organosilanol and/or a partial condensate thereof,

(Step 2) subjecting the organosilanols and/or partial condensates thereof to polycondensation reaction in an aqueous alkali solution or a mixed solution of the aqueous alkali solution and an organic solvent to obtain a dispersion of polyorganosiloxane fine particles, and

(Step 3) then drying the dispersion of the polyorganosiloxane fine particles.

Each of the steps will be explained below.

Step 1 is a step to partially or completely hydrolyze two kinds of organoalkoxysilanes represented by the above-described formulae (I) and (II) in the presence of an organic acid to obtain the corresponding organosilanols and/or partial condensates thereof.

Examples of the substituted or unsubstituted monovalent hydrocarbon group represented by  $R^1$  in the formulae (I) and (II) are the same monovalent hydrocarbon groups as in the R groups bonded to the silicon atoms in the polyorganosiloxane fine particles. In the case where an epoxy ring-containing group such as a  $\gamma$ -glycidoxypropyl group or a 3,4-epoxycyclohexylethyl group is contained as  $R^1$  in the organoalkoxysilane of the formula (I) or (II), part of the epoxy ring undergoes ring opening by the action of the organic acid which is a catalyst for hydrolysis or the alkali which is a catalyst for polycondensation, and especially where the catalyst for polycondensation is ammonia, the ring-opening reaction results in the formation of a nitrogen-containing



group. It should, however, be noted that the objects of the present invention are by no means impaired by such results.

In the formulae (I) and (II), examples of the substituted or unsubstituted alkyl groups represented by  $R^2$  include an alkyl group such as methyl, ethyl, propyl or butyl, and a substituted alkyl group such as methoxyethyl, ethoxyethyl or butoxyethyl. Preferred among these are methyl and ethyl, particularly methyl, from the standpoint of reaction rate.

Specific examples of the organotrialkoxysilane of the formula (I) include methyltrimethoxysilane, methyltriethoxysilane, methyltriisopropoxysilane, methyltris(methoxyethoxy)silane, ethyltrimethoxysilane, vinyltrimethoxysilane, vinyltris(methoxyethoxy)silane, phenyltrimethoxysilane,  $\gamma$ -chloropropyltrimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane and  $\gamma$ -mercaptopropyltrimethoxysilane. They may be used alone or in combination of two or more thereof.

Specific examples of the diorganodialkoxysilane of the formula (II) include dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane,

diphenyldiethoxysilane,  $\gamma$ -chloropropylmethyldimethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyldimethoxysilane and  $\gamma$ -glycidoxypropylmethyldimethoxysilane. Again, they may be used alone or in combination of two or more thereof.

The amount of the organoalkoxysilanes represented by the formulae (I) and (II) used in Step 1 is such that the amount of the diorganodialkoxysilane of the formula (II) is 0.01 to 2 mol per mol of the organotrialkoxysilane of the formula (I). If the amount of the organodialkoxysilane (II) exceeds 2 mols, it becomes difficult to obtain polyorganosiloxane fine particles having a homogeneous composition. Further, if the amount thereof is less than 0.01 mol, it is impossible to impart functionality by introduction of an organic group or to impart elasticity.

The hydrolysis reaction in Step 1 is conducted by using an aqueous solution of an organic acid as a catalyst dissolved in excess water.

Use of the organic acid as a catalyst is advantageous in that the reaction rate can be satisfactorily high and the polyorganosiloxane fine particles finally obtained contain no or, if any, a very small amount of impurities such as ionic substances, which restrict the use field of the product.

Examples of the organic acid include formic acid, acetic acid, propionic acid, monochloroacetic acid, oxalic acid and citric acid. Preferred are formic acid and acetic acid, from the standpoints that even a small amount thereof can effectively accelerate the hydrolysis reaction and also inhibit the partial condensation reaction of the polyorganosilanol formed.

The amount of the organic acid used varies depending on the kinds of the organoalkoxysilanes and also on the organic acid itself. However, the amount thereof is preferably in the range of from  $1 \times 10^{-3}$  to 1 part by weight, more preferably from  $5 \times 10^{-3}$  to 0.1 part by weight, per 100 parts by weight of the water used for the hydrolysis of the organoalkoxysilanes. If the amount of the organic acid is below  $1 \times 10^{-3}$  part by weight, the reaction cannot proceed sufficiently. On the other hand, if the amount thereof exceeds 1 part by weight, not only does the organic acid remain in the resulting reaction system as an

acid group in impurities at a high concentration, but also the organosilanols produced tend to undergo condensation.

The amount of the water used for the hydrolysis reaction is preferably from 2 to 10 mols per mol of the organoalkoxysilane. If the amount of the water is below 2 mols, the hydrolysis reaction cannot proceed sufficiently. If the amount thereof exceeds 10 mols, partial condensates of the organosilanols separate out and precipitate as a gel-like material.

The temperature of the hydrolysis is not particularly restricted and the hydrolysis may be conducted at room temperature or under heating. However, in order to obtain the organosilanols in high yield, the reaction is preferably conducted while the temperature is maintained at 5 to 80°C.

Step 2 is a step to obtain polyorganosiloxane fine particles through a polycondensation reaction from the organosilanols and/or partial condensates thereof as obtained in Step 1. This reaction in Step 2 is conducted in an aqueous alkali solution or in a mixed solution of the aqueous alkali solution and an organic solvent.

The alkali used herein means an agent whose aqueous solution shows basicity, and functions not only as a neutralizing agent to neutralize the organic acid used in Step 1 but also as a catalyst for the polycondensation reaction in Step 2. Examples of the alkali include metal hydroxides such

as lithium hydroxide, sodium hydroxide and potassium hydroxide; ammonia; and organic amines such as monomethylamine and dimethylamine. Preferred are ammonia and organic amines from the standpoint of not leaving even a slight amount of impurities which restrict the use field of the polyorganosiloxane fine particles. Particularly preferred is ammonia because of its low toxicity and easy removal.

The alkali is used in the form of an aqueous solution because it is easy to handle and control of the reaction is easy.

The alkali is used in an amount sufficient to neutralize the organic acid and to act effectively as a catalyst for the polycondensation reaction. For example, in the case where ammonia is used as the alkali, its amount is 0.05 part by weight or more per 100 parts by weight of water or a mixture of water and the organic solvent.

In Step 2, the organic solvent is preferably used in combination with an aqueous solution of the alkali from the standpoint of obtaining fine particles having an average particle diameter of 0.5  $\mu\text{m}$  or less and a specific surface area of 100  $\text{m}^2/\text{g}$  or more.

The organic solvent used is preferably water-soluble, and examples thereof include alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, diacetone alcohol; glycols such as ethylene glycol, propylene

glycol ; glycol ethers such as ethylene glycol monoethyl ether ; ketones such as acetone; and cyclic esters such as tetrahydrofuran, dioxane. They can be used alone or as mixtures thereof.

The polycondensation reaction in Step 2 is conducted by introducing into a reaction vessel the aqueous alkali solution or a mixed solution of the aqueous alkali solution and the organic solvent (hereinafter inclusively referred to as an "alkali solution"), and then adding thereto the organosilanols or partial condensates thereof (hereinafter inclusively referred to as "silanol compounds") obtained in Step 1 in the form of an aqueous solution or a solution prepared by diluting the aqueous silanol compound solution with water or the above-described organic solvent (hereinafter inclusively referred to as a "silanol solution"), thereby to bring the silanol compounds into contact with the alkali solution, followed by stirring or being allowed to stand, if desired and necessary.

The manner of adding the silanol solution to the alkali solution is not particularly limited.

The rate of the addition of the silanol solution is not particularly limited either. The optimum rate of addition can be determined, for example, by the kinds of the silanol compounds, whether or not the alkali solution contains an organic solvent, and the kind of the organic solvent, if used.

Specifically, for the purpose of obtaining polyorganosiloxane fine particles having a small average particle diameter, the silanol solution is added to the aqueous alkali solution over a period of preferably at least 5 minutes, more preferably from 10 to 240 minutes.

In the case where the silanol solution is added to an alkali solution containing an organic solvent, the addition is preferably completed within 5 minutes.

By conducting the polycondensation reaction as described above, polyorganosiloxane fine particles can be obtained as a gel-like dispersion having flowability or thixotropy in water or a mixed solution of water and an organic solvent.

The polyorganosiloxane fine particles of the present invention may be used in such a dispersion. Generally, however, the dispersion of the fine particles are further subjected to drying as Step 3. In the case of producing fine particles having a specific surface area of, for example,  $100 \text{ m}^2/\text{g}$  or more, Step 3 is required to include deaggregation treatment together with drying treatment, which deaggregates the fine particles to form separate, independent particles.

In the case where only the drying step is conducted in Step 3, an aggregate of particles can be obtained. In the case where the deaggregation is conducted together with drying in Step 3, the fine particles can be obtained in independent form.

The method for drying or deaggregating the above dispersion of the polyorganosiloxane fine particles is not particularly limited. However, it is necessary to dry the dispersion to such an extent that the volatile content of fine particle powder obtained by drying the above dispersion is reduced to 5 wt% or less, in order to obtain fine particles having a specific surface area of 100 m<sup>2</sup>/g or more or independent or spherical fine particles.

The drying and deaggregation treatment is generally conducted using a micron dryer (manufactured by Hosokawa Micron K.K., Japan), a thermo-jet dryer (manufactured by Seishinki Kigyo K.K., Japan) or the like.

The conditions of the above Steps 2 and 3 are summarized below in the light of the relationship to the average particle diameter of polyorganosiloxane fine particles.



**Step 3**  
**(drying and/or**  
**deaggregation)**

### Step 2 (at polycondensation reaction)

| Average particles diameter (μm) | Alkali solution       | Addition of silanol solution | Stirring period        | At the time of particle formation | State of dispersion              |
|---------------------------------|-----------------------|------------------------------|------------------------|-----------------------------------|----------------------------------|
| 5                               | Organic solvent rich  | Together (within 5 min)      | Until uniformly mixed  | Allowed to stand                  | Uniform thixotropy               |
| 10                              | Water                 | Dropwise (more than 5 min)   | Until particles formed | Stirring                          | Uniform flowability              |
| 15                              | Water/organic solvent | Together (within 5 min)      | Until uniformly mixed  | Allowed to stand                  | Particles partially precipitated |

Deaggregation together with drying drying

Drying, and deaggregation after drying is effective

Drying, and deaggregation after drying is effective

It should be noted, however, that the Table is an example of conditions which are summarised for easy explanation of the steps. For practical operation, further complicated conditions are imposed, and the conditions of Steps 2 and 3 should not be limited to the above.

The polyorganosiloxane fine particles obtained by the present invention have a small average particle diameter of 0.01 to 100  $\mu\text{m}$  and a spherical particle shape, so that the particles can be easily blended with and dispersed in various plastics. The average particle diameter of 0.01 to 20  $\mu\text{m}$  is more preferred from the standpoints of addition to plastics and dispersibility therein.

According to the process of the present invention, polyorganosiloxane fine particles containing various kinds of organic groups, which particles have been difficult to produce by conventional methods, can be obtained in a high yield and the thus-produced polyorganosiloxane fine particles can have a composition which is in good agreement with that of the raw materials used. Further, according to the process of the present invention, it is also possible to obtain polyorganosiloxane fine particles having a specific surface area of 100  $\text{m}^2/\text{g}$  or more.

The polyorganosiloxane fine particles obtained by the process of this invention are useful as a filler or additive for coatings, plastics, rubbers, paper or the like.

Particularly, the fine particles are suitable for use as an additive for improving surface slip properties of plastic films, a filler for transparent plastics or a reinforcing agent. Furthermore, the polyorganosiloxane fine particles having introduced therein organofunctional groups can be advantageously used for the surface modification of molded plastic articles or the like.

The present invention will now be explained in more detail by reference to the following Examples and Comparative Examples, but the Examples should not be construed to limit the scope of the invention. In the Examples, all percents, parts, ratios or the like are by weight unless otherwise indicated.

#### Evaluation Method

The properties of polyorganosiloxane fine particles were measured by the following evaluation methods.

Average particle diameter and shape:

Measured and observed by electron microscope

Specific surface area:

According to BET method

Bulk specific gravity:

Measured according to JIS K-5101

EXAMPLE 1

Step 1

Into a reaction vessel equipped with a thermometer, a reflux condenser and a stirrer was introduced 1,836 parts of water, and 1 part of acetic acid was then added thereto to give a uniform solution. To this solution were added 2,040 parts of methyltrimethoxysilane and 360 parts of dimethyldimethoxysilane, while stirring the solution at 30°C. As a result, hydrolysis proceeded and the temperature rose to 60°C in 60 minutes, thereby forming a transparent liquid reaction mixture. The reaction mixture was kept while stirring for 10 hours and then filtered, thereby obtaining a silanol solution.

Step 2

Into a reaction vessel equipped with a thermometer, a reflux condenser and a stirrer were introduced 1,560 parts of water and 40 parts of 28% aqueous ammonia, and the resulting mixture was kept at 25°C. To the mixture was added dropwise, with stirring, 400 parts of the silanol solution obtained in Step 1 over a period of about 10 minutes. After completion of the addition, stirring was continued for 16 hours, during which polymethylsiloxane fine particles separated out, whereby the reaction mixture was changed into a milky dispersion.

### Step 3

The dispersion obtained in Step 2 was subjected to centrifugal separation to precipitate fine particles and the resulting precipitate was taken out and dried in a dryer at 200°C for 24 hours. Thus, 110 parts of white fine particles were obtained. This yield corresponded to 94.8% of the theoretical yield based on the methyltrimethoxysilane.

Examination with an electron microscope revealed that almost all the particles were spherical and the particles had a maximum particle diameter of 2  $\mu\text{m}$ , a minimum particle diameter of 0.5  $\mu\text{m}$  and an average particle diameter of 1  $\mu\text{m}$ .

The above-obtained fine particles were put in a porcelain crucible and pyrolyzed at 900°C in air. As a result, the pyrolysis residue weighed 87.0% of the fine particles, and this value was close to the theoretical value, 87.4%, for the oxidation pyrolysis of polymethylsiloxane into silicon dioxide. Upon X-ray analysis, the pyrolysis residue was ascertained to be amorphous silica. It was confirmed from these analytical results that the white fine particles obtained above were polymethylsiloxane.

### EXAMPLE 2

Polyorganosiloxane fine particles were obtained in the same manner as in Example 1 except that the polycondensation in Step 2 was conducted as follows.

Into a reaction vessel equipped with a thermometer, a reflux condenser and a stirrer were introduced 300 parts of methanol, 300 parts of water and 15 parts of 28% aqueous ammonia, and the resulting mixture was kept at 25°C. To the mixture was added, with stirring, 300 parts of the silanol solution as obtained in Step 1 of Example 1 over a period of about 10 seconds. After the addition, the resulting mixture was stirred for about 60 seconds. The stirring was stopped and the resulting mixture was allowed to stand for 24 hours. As a result, polyorganosiloxane fine particles were formed and sedimented. The fine particles thus sedimented were treated in the same manner as in Step 3 of Example 1, thereby obtaining polyorganosiloxane fine particles having a maximum particle diameter of 15  $\mu\text{m}$ , a minimum particle diameter of 5  $\mu\text{m}$  and an average particle diameter of 8  $\mu\text{m}$ . Upon examination with an electron microscope, almost all the particles were found to be spherical.

### EXAMPLE 3

#### Step 1

A silanol solution was obtained in the same manner as in Example 1 except for using 2,025 parts of water, 0.75 part of acetic acid, 1,530 parts of methyltrimethoxysilane and 1,350 parts of dimethyldimethoxysilane.

Step 2

Polyorganosiloxane fine particles were obtained in the same manner as in Example 2 except for using 300 parts of the silanol solution as obtained in Step 1 above, 600 parts of water and 15 parts of 28% aqueous ammonia.

Step 3

The thus-obtained fine particles were treated in the same manner as in Step 3 of Example 1, thereby obtaining almost spherical polyorganosiloxane fine particles having a maximum particle diameter of 5  $\mu\text{m}$ , a minimum particle diameter of 2  $\mu\text{m}$  and an average particle diameter of about 3  $\mu\text{m}$ .

EXAMPLE 4

The same procedures as in Example 3 were repeated except that in Step 2, 300 parts of the silanol solution as obtained in Step 1 of Example 3 were used, and a mixed solution of 450 parts of water and 150 parts of methanol was used in place of 600 parts of water.

As a result, polyorganosiloxane fine particles were obtained in the form of aggregates composed of a large number of spherical particles having a particle diameter of 4 to 8  $\mu\text{m}$ . The aggregates were then deaggregated by means of a jet mill, thereby obtaining fine particles having an average particle diameter of 5  $\mu\text{m}$ .

COMPARATIVE EXAMPLE 1

250 Parts of the same mixture of alkoxysilanes as used in Example 1 were directly (without hydrolysis) added to a mixed

solution of 1,725 parts of water not containing an organic solvent and 100 parts of 28% aqueous ammonia over a period of about 10 seconds in the same manner as in Step 2 of Example 3. The resulting mixture was then stirred and allowed to stand in the same manner as in Example 2. After the treatment, it was observed that an oily liquid was floating on the surface of the reaction mixture and there was a large mass of gel at the bottom of the reaction vessel.

#### EXAMPLE 5

##### Step 1

A silanol solution was obtained in the same manner as in Step 1 of Example 1 except that in place of 360 parts of dimethyldimethoxysilane as used in Example 1, 660 parts of  $\gamma$ -glycidoxypropylmethyldimethoxysilane were used.

##### Step 2

Into a reaction vessel equipped with only a stirrer were introduced 5,400 parts of methanol and 90 parts of 28% aqueous ammonia. To the mixture was added 2,700 parts of the silanol solution as obtained in Step 1, and the resulting mixture was stirred for about 5 minutes to give a uniform mixture. The stirring was then stopped and the mixture was allowed to stand so as to proceed a reaction. After the stirring was stopped, the viscosity of the reaction mixture increased gradually and, in 3 hours, the mixture changed into a gel-like dispersion having no flowability but having thixotropy.



### Step 3

The dispersion as obtained in Step 2 was deaggregated with a thermo-jet dryer while drying the dispersion in a hot air at 150°C.

As a result of the treatments in Steps 1 to 3 above, there were obtained polyorganosiloxane fine particles having a specific surface area of 450 m<sup>2</sup>/g, a bulk specific gravity of 35 g/l and a volatile content, as measured through 150°C-drying treatment for 60 minutes, of 2% or less.

### EXAMPLE 6

The same procedures as in Example 5 were repeated except that 45 parts of N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane was used in Step 2 in place of 45 parts in 90 parts of 28% aqueous ammonia, to obtain polyorganosiloxane fine particles having a specific surface area of 550 m<sup>2</sup>/g and a bulk specific gravity of 300 g/l.

### EXAMPLE 7

A silanol solution was prepared in the same manner as in Step 1 of Example 1 except that the amount of dimethyldimethoxysilane was changed to 120 parts and the amount of water was changed to 1,692 parts.

Steps 2 and 3 were the same as in Example 5 to obtain polyorganosiloxane fine particles.

The polyorganosiloxane fine particles thus obtained has maximum particle diameter of 0.06 μm, a minimum particle

diameter of 0.03  $\mu\text{m}$ , an average particle diameter of 0.04  $\mu\text{m}$  and a specific surface area of 450  $\text{m}^2/\text{g}$ .

#### EXAMPLE 8

Polyorganosiloxane fine particles were obtained by the same manner as in Example 1 except that 1,836 parts of methyltrimethoxysilane, 222 parts of vinyltrimethoxysilane and 360 parts of dimethyldimethoxysilane were used.

The fine particles thus obtained were subjected to the same treatment as in Step 3 of Example 1 to obtain substantially spherical polyorganosiloxane fine particles having a maximum particle diameter of 1.5  $\mu\text{m}$ , a minimum particle diameter of 0.5  $\mu\text{m}$  and an average particle diameter of about 0.8  $\mu\text{m}$ .

#### EXAMPLE 9

Polyorganosiloxane fine particles were obtained in the same manner as in Example 2 except that 1,600 parts of water were used in Step 2 in place of 300 parts of methanol and 300 parts of water, using 1,836 parts of methyltrimethoxysilane, 298 parts of phenyltrimethoxysilane, 3 parts of acetic acid and 2,025 parts of water.

The fine particles thus obtained were subjected to the same treatment as in Step 3 of Examples 1 to obtain spherical fine particles having a maximum particle diameter of 5  $\mu\text{m}$ , a minimum particle diameter of 0.8  $\mu\text{m}$  and an average particle diameter of about 2  $\mu\text{m}$ .

#### EXAMPLE 10

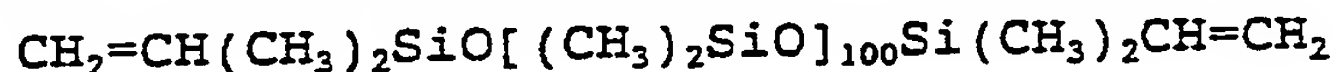
Silanol solution was obtained in the same manner as in Step 1 of Example 1 except for using 2,064 parts of hexyltrimethoxysilane, 240 parts of dimethyldimethoxysilane and 2 parts of acetic acid.

Steps 2 and 3 were the same as in Example 4 to obtain polyorganosiloxane fine particles.

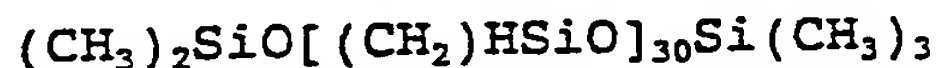
The polyorganosiloxane fine particles thus obtained had a maximum particle diameter of 5  $\mu\text{m}$ , a minimum particle diameter of 0.4  $\mu\text{m}$  and an average particle diameter of 1.2  $\mu\text{m}$ .

#### COMPARATIVE EXAMPLE 2

To 100 parts of dimethylpolysiloxane having vinyl group at both terminals, represented by an average composition formula



were added 2 parts of methylhydrogenpolysiloxane represented by an average composition formula



an isopropyl alcohol solution of platonic acid chloride in an amount of 10 ppm, calculated as platinum, based on the total weight of the siloxanes, and 0.1 part of 3-methyl-1-butyn-3-ol.

The resulting mixture was atomized into a spray drier having a diameter of 2 m and a height of 4 m with a rotating nozzle and cured to obtain a cured powder at a rate of 50

kg/hr. The inlet temperature of hot air in spray drier was 230°C.

The cured product was collected by a cyclon. As a result of examination with a scanning type electron microscope, the cured product was a spheriform rubber composed of particles having a particle diameter of 2 to 30  $\mu\text{m}$ , and the spherical rubber powder was a bulk product having a diameter of 3 mm or less.

The results obtained above are shown in the Table below together with the properties of the fine particles obtained.

TABLE

|  | <u>Examples</u> |          |          |          |          |          |
|--|-----------------|----------|----------|----------|----------|----------|
|  | <u>1</u>        | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> | <u>6</u> |
| <u>Step 1</u>  |                 |          |          |          |          |          |
| Trialkoxysilane:<br>(parts by weight)                    |                 |          |          |          |          |          |
| Methyltri-<br>methoxysilane                              | 2,040           | 2,040    | 1,530    | 1,530    | 2,040    | 2,040    |
| Vinyltri-<br>methoxysilane                               | -               | -        | -        | -        | -        | -        |
| Phenyltri-<br>methoxysilane                              | -               | -        | -        | -        | -        | -        |
| Hexyltri-<br>methoxy-silane                              | -               | -        | -        | -        | -        | -        |
| Dialkoxysilane<br>(parts by weight)                      |                 |          |          |          |          |          |
| Dimethyldi-<br>methoxysilane                             | 360             | 360      | 1,350    | 1,350    | -        | -        |
| $\gamma$ -glycidoxy-<br>propylmethyl-<br>dimethoxysilane | -               | -        | -        | -        | 660      | 660      |
| Acetic acid<br>(parts by weight)                         | 1               | 1        | 0.75     | 0.75     | 1        | 1        |
| Water<br>(parts by weight)                               | 1,836           | 1,836    | 2,025    | 2,025    | 1,836    | 1,836    |
| T/D*   | 15/3            | 15/3     | 5/5      | 5/5      | 15/3     | 15/13    |

\* Mol ratio of trialkoxysilane and dialkoxysilane -

TABLE (to be continued)

|  | <u>Examples</u> |          |          |           | <u>Comparative<br/>Example 1</u> |
|--|-----------------|----------|----------|-----------|----------------------------------|
|  | <u>7</u>        | <u>8</u> | <u>9</u> | <u>10</u> |                                  |
| <u>Step 1</u>  |                 |          |          |           |                                  |
| Trialkoxysilane:<br>(parts by weight)                    |                 |          |          |           |                                  |
| Methyltri-<br>methoxysilane                              | 2,040           | 1,836    | 1,836    | -         | 212.5                            |
| Vinyltri-<br>methoxysilane                               | -               | 222      | -        | -         | -                                |
| Phenyltri-<br>methoxysilane                              | -               | -        | 298      | -         | -                                |
| Hexyltri-<br>methoxy-silane                              | -               | -        | -        | 2,064     | -                                |
| Dialkoxysilane<br>(parts by weight)                      |                 |          |          |           |                                  |
| Dimethyldi-<br>methoxysilane                             | 120             | 360      | 360      | 240       | 37.5                             |
| $\gamma$ -glycidoxy-<br>propylmethyl-<br>dimethoxysilane | -               | -        | -        | -         | -                                |
| Acetic acid<br>(parts by weight)                         | 1               | 1        | 3        | 2         | -                                |
| Water<br>(parts by weight)                               | 1,692           | 1,836    | 2,025    | 1,836     | -                                |
| T/D*   | 15/1            | 15/3     | 15/3     | 15/3      | 15/3                             |

TABLE (Cont'd)

|   | Examples  |           |           |                          |           |           |
|---|-----------|-----------|-----------|--------------------------|-----------|-----------|
|   | <u>1</u>  | <u>2</u>  | <u>3</u>  | <u>4</u>                 | <u>5</u>  | <u>6</u>  |
| <u>Step 2</u>   |           |           |           |                          |           |           |
| 28% Ammonia aqueous solution (parts)  | 40        | 15        | 15        | 15                       | 90        | 45        |
| Water   | 1,560     | 300       | 600       | 450                      | -         | -         |
| Methanol (parts)  | -         | 300       | -         | 150                      | 5,400     | 5,400     |
| N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyl-dimethoxysilane (parts) | -         | -         | -         | -                        | -         | 45        |
| Silanol solution (parts)  | 400       | 300       | 300       | 300                      | 2,700     | 2,700     |
| <u>Fine Particle Formed</u>   |           |           |           |                          |           |           |
| Dry weight (parts)  | 110       | 86        | 88        | 81                       | 800       | 810       |
| Yield(%)  | 94.8      | 99        | 85.8      | 83.5                     | 82.3      | 80.5      |
| Shape   | Spherical | Spherical | Spherical | Spherical<br>(Aggregate) | Spherical | Spherical |

TABLE (Cont'd)

|   | Examples  |           |           |           | Comparative    |
|---|-----------|-----------|-----------|-----------|----------------|
|   | <u>7</u>  | <u>8</u>  | <u>9</u>  | <u>10</u> | <u>Example</u> |
| <u>Step 2</u>   |           |           |           |           |                |
| 28% Ammonia aqueous solution (parts)  | 90        | 40        | 15        | 15        | 100            |
| Water   | -         | 1,560     | 1,600     | 450       | 1,725          |
| Methanol (parts)  | 5,400     | -         | -         | 150       | -              |
| N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropylmethyl-dimethoxysilane (parts) | -         | -         | -         | -         | -              |
| Silanol solution (parts)  | 2,700     | 400       | 300       | 300       | -              |
| <u>Fine Particle Formed</u>   |           |           |           |           |                |
| Dry weight (parts)  | 680       | 114       | 94        | 88        | -              |
| Yield(%)  | 90.0      | 85        | 90        | 80        | -              |
| Shape   | Spherical | Spherical | Spherical | Spherical | *              |

\* Fine particles were not formed, and oily layer and gel bulk were formed.



APPLICATION EXAMPLE

0.5 Part of the fine particles obtained in Example 1 and 99.5 parts of a polypropylene powder (melting point: 162°C) were mixed with Henschel mixer. The resulting mixture was extruded and pelletized with a twin-screw extruder at 250°C to obtain chips composed of the composition above.

The chips were co-extruded using a two layer metal head outlet at 250°C, maintained at 40°C and then cooled to solidify, thereby obtaining a two layer film.

The film was heated to 140°C, stretched at a stretching ratio of 5 times in a machine direction and then immediately cooled to 40°C.

The film was introduced into a tenter maintained at 160°C, and then stretched at a stretching ratio of 8 times in a width direction.

The thickness of the film after stretching treatment was 20  $\mu\text{m}$ , and the layer thickness of the ethylene-propylene random copolymer therein was 3  $\mu\text{m}$ .

The film obtained was transparent. When the films were rubbed against each other, they showed a good lubricating property. Further, even when the films were rubbed against each other repeatedly, the film surface did not whiten, and transparency was maintained.

COMPARATIVE APPLICATION EXAMPLE

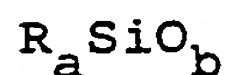
A film was prepared in the same manner as in Application Example above except that the fine particles obtained in Comparative Example 2 were used in place of the fine particles obtained in Example 1.

When the films obtained were rubbed against each other, the lubricating property was small, and when the number of rubbings was increased, the film surface whitened.

Observation of the whitened film surface with a scanning type electron microscope indicated that the fine particles obtained in Comparative Example 2 had separated from the film.

CLAIMS

1. Polyorganosiloxane fine particles having an average composition represented by the formula,



wherein R represents a substituted or unsubstituted monovalent hydrocarbon group, and a and b are numbers defined by the formulae  $1 < a \leq 1.7$ ,  $1 < b < 1.5$  and  $a + 2b = 4$ , said fine particles having an average particle diameter of from 0.01 to 100  $\mu\text{m}$ , and being of spherical form.

2. Polyorganosiloxane fine particles as claimed in claim 1, wherein R is an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, an alkenyl group or a substituted hydrocarbon group.

3. Polyorganosiloxane fine particles as claimed in claim 1 or 2, wherein the average particle diameter is from 0.01 to 20  $\mu\text{m}$ .

4. Polyorganosiloxane fine particles as claimed in claim 1, 2 or 3 and having a volatile content of 5 wt% or less.

5. A process for producing polyorganosiloxane fine particles which comprises the steps of:

partially or completely hydrolyzing in the presence of an organic acid a mixture of an organotrialkoxysilane represented by the formula (I)



wherein  $R^1$  represents a substituted or unsubstituted monovalent hydrocarbon group and  $R^2$  represents a substituted or

unsubstituted alkyl group, and a diorganodialkoxysilane represented by the formula (II)



wherein  $R^1$  and  $R^2$  are as defined above, the amount of the diorganodialkoxysilane being from 0.01 to 2 mols per mol of the organotrialkoxysilane, thereby to obtain an organosilanol and/or a partial condensate thereof, and

subjecting said organosilanols and/or partial condensates thereof to polycondensation reaction in an aqueous alkali solution or a mixed solution of the aqueous alkali solution and an organic solvent, thereby to obtain a dispersion of polyorganosiloxane fine particles.

6. A process as claimed in Claim 5 and additionally comprising the step of drying the dispersion to separate said polyorganosiloxane fine particles from the dispersion.

7. A process as claimed in claim 5 or 6, wherein the organic solvent is used in an amount of from 1 to  $10^{-3}$  part by weight per 100 parts by weight of water used for hydrolysis.

8. A process as claimed in claim 5, 6 or 7, wherein the amount of water used for hydrolysis is from 2 to 10 mols per mol of the organotrialkoxysilane.

9. A process as claimed in any one of claims 5 to 8, wherein the hydrolysis is conducted at a temperature of from 5 to 60°C.

10. A process as claimed in any one of claims 5 to 9 wherein the alkali is a metal hydroxide, ammonia or an organic amine.

11. A process as claimed in any one of claims 5 to 10 wherein the alkali is used in an amount of from 0.05 parts by weight or more per 100 parts by weight of water or a mixture of water and an organic solvent.

12. A process as claimed in any one of claims 5 to 11, wherein the organic solvent comprises one or more solvents selected from alcohols, glycols, glycol ethers, ketones and cyclic ethers.

13. A process as claimed in any one of claims 5 to 12, wherein the polycondensation reaction is conducted in such a manner that the organosilanol and/or partial condensates thereof are added to the aqueous alkali solution or to the mixed solution of the aqueous alkali solution and the organic solvent.

14. A process as claimed in any one of claims 6 to 13, wherein the drying is conducted together with deaggregation.

15. Polyorganosiloxane fine particles substantially as herein described with reference to any of the foregoing Examples 1 to 10.

16. Polyorganosiloxane fine particles as claimed in claim 1 and substantially as hereinbefore described.

17. A process for producing polyorganosiloxane fine particles substantially as herein described with reference to any one of the foregoing Examples 1 to 10.

18. A process for producing polyorganosiloxane fine particles as claimed in claim 5 and substantially as hereinbefore described.

19. Polyorganosiloxane fine particles when produced by a process as claimed in any one of claims 5 to 14, claim 17 or claim 18.

20. The features herein described, or their equivalents in any novel, patentable selection.